IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of	
Applicant(s)	: A. Faur-Ghenciu
Serial No.	: 10/617,146
Filed	: July 10, 2003
Title	: HIGH ACTIVITY WATER GAS SHIFT CATALYSTS BASED ON PLATINUM GROUP METALS AND CERIUM-CONTAINING OXIDES
Docket No.	: GMC 0025 PA / 42320.29/GP-3
Examiner	: K. Handal
Art Unit	: 1764

CERTIFICATE OF FACSIMILE TRANSMISSION
I hereby certify that this paper is being facsimile transmitted to the Patent and Trademark Office (Fax No. 571/273-8300) on December 20, 2006.

Patricia L. Prior
Patricia L. Prior, Attorney Reg No. 33,758

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

DECLARATION OF ANCA FAUR-GHENCIU, NATHAN E. TRUSTY, MARK R. FEAVIOUR, JESSICA G. REINKINGH, PHILLIP SHADY, AND PAUL J. ANDERSEN UNDER 37 C.F.R. 1.131

Anca Faur-Ghenciu, Nathan E. Trusty, Mark R. Feaviour, Jessica G. Reinkingh, Phillip Shady, and Paul J. Andersen, the applicants in the above-identified patent application, declare as follows:

1. We are the inventors of claims 1-61 of the above-identified patent application and inventors of the subject matter described and claimed therein.

2. Prior to March 28, 2002, we reduced the present invention to practice as evidenced by Exhibits A-C attached hereto.

3. Exhibit A is a copy of a Record of Invention prepared with respect to the present invention. The Record of Invention includes a brief description of the invention, testing conditions, various catalyst formulations, results and conclusions, and references to supporting data.

4. Exhibit B is a copy of pages 17-30 of Laboratory Notebook No. 1875. These pages show the preparation of several catalysts of the present invention as well as comparison examples. Pages 23, 25, and 29 are referred to on page 4 of the Record of Invention.

5. Exhibit C is a copy of an email from Peter Gray of Johnson Matthey PLC to James Saller of General Motors Corporation, the assignee of the present invention, with an attachment forwarding the Record of Invention for the present invention.

6. Each of the dates deleted from Exhibits A-C is prior to March 28, 2002. All work relating to the conception and reduction to practice of this invention was carried out in a WTO country.

The declarants further state that the above statements were made with the knowledge that willful false statements and the like are punishable by fine and/or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of this application or any patent resulting therefrom.

Date: __________	See attached sheet Anca Faur-Ghenciu
Date: __________	See attached sheet Nathan E. Trusty
Date: __________	See attached sheet Mark. R. Feaviour
Date: __________	See attached sheet Jessica G. Reinkingh

Serial No. 10/617,146
Docket No. GMC 0025 PA/40320.29/GP-3

Date: ____________________ See attached sheet
Phillip Shady

Date: ____________________ See attached sheet
Paul J. Andersen

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Serial No. 10/617146
Docket No. GMC 0025 PA/40320.29/GP-3

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Date: Dec 14, 2006 — A Faur Ghenciu
Anca Faur-Ghenciu

Date: ____________ ____________
Nathan E. Trusty

Date: ____________ ____________
Mark. R. Feaviour

Date: ____________ ____________
Jessica G. Reinkingh

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Date: ________________ Anca Faur-Ghenciu

Date: 12/13/06 Nathan E. Trusty Nathan Trusty

Date: ________________ Mark. R. Feaviour

Date: ________________

Serial No. 10/617146
Docket No. GMC 0025 PA/40320.29/GP-3

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Date: ____________________ ____________________
Anca Faur-Ghenciu

Date: ____________________ ____________________
Nathan E. Trusty

Date: 13th Dec 2006 M. Feav
Mark. R. Feaviour

Date: ____________________ ____________________
Jessica G. Reinkingh

Serial No. 10/617146
Docket No. GMC 0025 PA/40320.29/GP-3

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Date: ____________ ____________
Anca Faur-Ghenciu

Date: ____________ ____________
Nathan E. Trusty

Date: 12/13/2007 ____________
Mark R. Reaviour

Date: ____________ ____________
Jessica G. Reinkingh

Serial No. 10/617146
Docket No. GMC 0025 PA/40320.29/GP-3

Date: 12/13/2006

Phillip Shady

Phillip Shady

Date: ______________

Paul J. Andersen

Serial No. 10/617146
Docket No. GMC 0025 PA/40320.29/GP-3

Date: ____________________

Phillip Shady

Date: December 13, 2006

Paul J. Andersen

Paul J. Andersen

JM
Johnson Matthey Fuel Cells
the power within

Exhibit "A"

RECORD OF INVENTION

Title of Invention: High Activity Water Gas Shift Catalysts Based on Promoted Platinum Group Metals - Ceria-containing Oxides

Record Written by: Anca Ghenciu

Date Record Written: .

Brief Description of Invention:
In the catalyzed water gas shift (WGS) reaction, the high activity WGS catalyst systems consisting of 1-4% platinum, or palladium, or platinum-palladium, or platinum-iridium, dispersed on or in the lattice of ceria-zirconia or ceria-lanthana mixed oxides with various ratios ceria-zirconia or ceria-lanthana, respectively, said catalysts including a 0.1%-1% promoter comprising of one or more alkali or alkaline-earth metals selected from the group of cesium, lithium, rubidium, potassium, or magnesium, strontium, barium, said catalyst including support dopants such as lanthanum, praseodymium, neodymium, all said catalysts tested in the presence of carbon monoxide, water, carbon dioxide and hydrogen, with best catalytic performance between 200°-400°C, preferably 250°-375°C. The invention also relates to the use of said catalysts as coated on monolithic supports for the WGS reaction.

Catalyst testing: fixed bed reactor, 1 g catalyst and 1 g cordierite 45-60 mesh, under the following reaction conditions: 8%CO, 30%H2O, 10%CO2, 32.5%H2, 1%CH4, balance N2, in a fixed bed reaction system, at 67,500 cc/g cat /hr weight hourly space velocity, between ~150° and ~600°C. Test results in each case (Examples) to be written.

Results and conclusions:

1. The ceria-zirconia mixed oxides show improved catalytic performance over ceria-lanthana, also over ceria- or zirconia-only. The ceria-zirconia catalysts of this invention show a decrease in the onset temperature of the WGS reaction (light-off temperature). Possible reasons for the improved catalytic activity conferred by ceria-zirconia mixed oxides:

- High thermal stability therefore improved durability/long-term stability conferred by the mixed oxide phase.
- Improved water adsorption properties compared to ceria-only supports (here citation of previously known 1%Pt/CeO2 catalyst), yet while keeping the oxygen mobility as conferred by ceria.
- Higher metal dispersion on ceria-zirconia mixed oxides than on ceria when the same method of metal deposition is used.
- Optimum ceria: zirconia ratio for the oxides studied ~ 20:80. Advantage of high Zr:Ce ratio perhaps due to improved water adsorption properties, that may also reflect in a better durability. A ceria content is necessary, since Pt/zirconia has poorer performance.

2. All platinum-ceria-zirconia mixed oxides of this invention show better activity than palladium,

platinum-palladium, or platinum-iridium catalysts in combination with the same oxides and prepared in the same manner. Platinum formulations offer advantage over palladium formulations based on the temperature difference between the onset of WGS and the onset of methanation; the no-methanation window for WGS reaction is wider in the case of Pt catalysts than for Pd formulations.

3. For the unpromoted formulations, methane formation is seen to a small extent at temperatures higher than 350°C under the testing conditions. The alkali and alkaline-earth promoters reduce the extent of methanation (conversion to methane formation) and/or shift the onset of methanation to higher temperatures.

4. Role of alkali and alkaline-earth promoters

- Improve the water adsorption/chemisorption properties of the oxidic support (also known from the technical literature as promoters for several partial oxidations and epoxidations). A more pronounced increase in the catalytic activity is seen in the case of Ce-rich mixed oxides than in the case of Zr-rich or La- rich ceria-containing mixed oxides.
- Reduce the extent of methanation. The temperature corresponding to the onset of methanation is higher in the case of Li than in the case of Cs (see "3" above).
- An improvement consisting of more than 50°C decrease in the temperature corresponding to the maximum catalytic activity is obtained with Cs- or Li/2%Pt/CeO2-ZrO2 (58:42 wt%) compared to the unpromoted formulation, 2%Pt/CeO2-ZrO2 (58:42 wt) or the known to the art Pt/CeO2.

5. Pt/Zr-rich ceria-zirconia formulations, even when unpromoted with alkali, show the same high activity as the alkali-promoted Pt/stoichiometric oxide, possibly due to improved water chemisorption with the increase in Zr content. The difference between the two may consist in long-term performance and durability.

6. Role of chosen dopants

- La, Pr, Nd improve the thermal stability of the support. Some reduction in activity seen in some cases.

Perhaps to also cover (or **publication**):
Impact of catalyst preparation method and material properties on catalyst performance, role of the metal-oxide interface in the catalytic activity: Pt-O-CeOx-ZrOx, continuum phase.

Novelty of the Invention:

Under the reaction conditions chosen for testing: **1.** Very high activity catalysts comprised of Pt, Pt-Pd, Pt-Ir/ceria-zirconia mixed oxides with different CeO2:ZrO2 ratios for medium temperature range WGS reaction, 200-400°C, preferably 300°-375°C. **2.** 1-4%Pt supported on ceria-zirconia mixed oxides show higher WGS activity than the similarly prepared Pt catalysts supported on either ceria-only or on zirconia-only, for the same Pt content. **3.** For Pt/ceria-zirconia catalysts, a Zr-rich formulation (i.e., CeO2-ZrO2 20:80, wt%) shows higher WGS activity than the stoichiometric oxide (CeO2:ZrO2 58:42, wt%) and also than a Ce-rich oxide (i.e., CeO2:ZrO2 70:30, wt%), but also than the Zr-only formulations. **4.** Cesium and Lithium promotion of the Pt/ceria-zirconia catalysts leads to further improvement in the WGS activity, at temperatures lower than in the case of the unpromoted catalysts. Over 50°C decrease in the temperature corresponding to the maximum catalytic activity is obtained with Cs- or Li/2%Pt/CeO2-ZrO2 (58:42

wt%) compared to the unpromoted formulation, 2%Pt/CeO_2-ZrO_2 (58:42 wt) or the known to the art Pt/CeO_2. **5.** The effect of promoters in the increase in activity is more pronounced in the case of Ce-rich formulations than for the Zr-rich formulation. **6.** The ceria-zirconia ratio is estimated to play a role in durability. **7.** For all CeO_2-ZrO_2 formulations studied, the alkaline metal promotion contributes to the reduction in methane formation. **8.** Promotion with Li shifts the onset of methanation to slightly higher temperatures than the promotion with Cs.

Benefit of Invention:

1. Catalyst formulations with very high catalytic activity for WGS reaction at medium temperature (300°-375°C), for the production of hydrogen. High catalytic activity with no methane formation below 350°C and minimum methane formation at temperatures higher than 350°C, in the presence of Pt/ceria-zirconia or Pt/ceria-lanthana mixed oxides, and thier alkali- or alkaline-earth promoted formulations. **2.** Improved catalytic activity with Cs- and Li-promoted Pt dispersed on/in CeO_2-ZrO_2 mixed oxides, at lower temperatures and with higher activity and selectivity than for Pt dispersed on CeO_2 or ZrO_2 only. **3.** Improved catalytic activity for WGS with high Zr/Ce ratios. **4.** Reduction in the methanation activity obtained in the presence of alkali-promoted formulations. **5.** Thermally stable catalytic materials based on the high thermal stability of the Ce-Zr mixed oxides. **6.** Possible improved thermal durability through the use of support dopants: Nd, Pr, La.

References to Supporting Work *(e.g. Lab Notebook Number)*:

1757-86-243	1%Pd/[90(CeO_2-ZrO_2 20:80)-10(Al_2O_3)]
1757-113-243C	1%Pd/[90(CeO_2-ZrO_2 20:80)-10(Al_2O_3)]
1757-93-253	1%Pd/[80(La_2O_3-CeO_2 60:20)-20(Al_2O_3)]
1757-131-1	1%Pd/75%La_2O_3-25%CeO_2
1757-131A2	(1%Pd-0.5%Pt)/75%La_2O_3-25%CeO_2
1757-133-4	(1%Pt-0.5%Cs)/75%La_2O_3-25%CeO_2
1757-139-2	1%Pt/75%La_2O_3-25%CeO_2
1757-136-1	1%Pd/25%La_2O_3-75%CeO_2
1757-137-2	(1%Pd-0.5%Pt)/ 25%La_2O_3-75%CeO_2
1757-141-1	(1%Pt-0.5%Cs)/ 25%La_2O_3-75%CeO_2
1757-140-1	1%Pt/ 25%La_2O_3-75%CeO_2
1757-143-14	(1%Pt-0.5%Cs)/CeO_2
1757-161A	0.2%Cs/2%Pt/CeO_2 –
1875-009	0.2%CsHPA/2%Pt/CeO_2
1757-164B	0.2%Ir/2%Pt/CeO_2 –

1757-159B	2%Pt/LaOx-CeO2 –
1875-010	0.2%CsHPA/2%Pt/LaOx-CeO2
1757-160B	0.2%Cs/2%Pt/La-CeO2 –
1757-161B	2%Pt/CeO2-ZrO2 (58:42 wt) –
1757-168A	2%Pt/CeO2-ZrO2 (19.6 : 80.4 wt) –
1757-186	0.2%Cs/2%Pt/CeO2-ZrO2 (19.6 : 80.4 wt) –
1757-163B	0.2%Cs/2%Pt/ CeO2-ZrO2 (58:42 wt) –
1757-166B	(2%Pt-0.2%Cs)/CeO2-ZrO2 (58:42 wt) (c) –
1757-167B	0.2%Cs/2%Pt/ CeO2-ZrO2 (58:42 wt) (cc) –
1757-168B	2%Pt/CeO2-ZrO2 (70.5 : 29.5 wt) –
1757-167A	2%Pt/CeO2-ZrO2-La2O3 (54.4 : 40.6 : 3.8 wt) –
1757-173A	repeat of 1757-166B –
1757-173B	(2%Pt-0.2%Cs)/CeO2-ZrO2 (58:42 wt) –
1757-166A	2%Pt/ CeO2-ZrO2 (58:42 wt) (c) – to be compared with 1757-161B - .
1757-177	2%Pt/0.2%Cs/CeO2-ZrO2 (58:42 wt) –
1757-175	2%Pt/0.2%Cs/CeO2-ZrO2 (58:42 wt) (c) –
1757-179	same as 1757-163B –
1757-181A	2%Pt/CeO2-ZrO2-La2O3-Nd2O3 (20 : 73.5 : 1.5 : 5 wt) –
1757-181B	2%Pt/CeO2-ZrO2-La2O3-Nd2O3 (20 : 73.5 : 1.5 : 5 wt) (c) –
1757-188B	2%Pt/(c) CeO2-ZrO2 (58:42 wt) –
1757-188A	2%Pt/CeO2-FeOx –
1757-189A	2%Pt/CeO2-ZrO2 (58 : 42 wt) (tp) –
1757-189B	2%Pt/CeO2-ZrO2 (19.6 : 80.4 wt) (tp) –
1757-193B	repeat of 1757-188B –
1875-023	xPt/CeOx-ZrOx -
1875-025	ZrO2- - Pt-CeOx
1875-029	2%Pt-ZrO2 – CeO2 (42:58) –
1757-207A	2%Pt/ZrO2 – July 01, 2001
1757-207B	0.2%Cs/2%Pt/(c) CeO2-ZrO2 (58:42 wt) –

1944-005	0.1%Cs/2%Pt/CeO2-ZrO2 (58 : 42 wt)
1944-007	0.5%Cs/2%Pt/CeO2-ZrO2 (58 : 42 wt)
1944-009	1%Cs/2%Pt/CeO2-ZrO2 (58 : 42 wt)
1944-013	1%Li/2%Pt/CeO2-ZrO2 (58 : 42 wt)
1944-015	0.5%Li/2%Pt/CeO2-ZrO2 (58 : 42 wt)
1944-065	1%Pt/2%Li/CeO2-ZrO2 (58 : 42 wt)
1944-067	0.2%Li/2%Pt/CeO2-ZrO2 (58 : 42 wt)
1944-069	5%Li/1%Pt/CeO2-ZrO2 (58 : 42 wt)
1944-073	1%Li/1%Pt/CeO2-ZrO2 (58 : 42 wt)
1944-075	2%Li/1%Pt/CeO2-ZrO2 (58 : 42 wt)
1944-051	0.2%Ba/2%Pt/CeO2-ZrO2 (58:42 wt) –
1944-053	0.2%K/2%Pt/CeO2-ZrO2 (58:42 wt) –
1944-055	0.2%Sr/2%Pt/CeO2-ZrO2 (58:42 wt) –
1944-049	0.2%Y/2%Pt/CeO2-ZrO2 (58 : 42 wt) –

Contributors to the Invention: A. Ghenciu, N. Trusty, M. Feaviour, J Reinkingh, P. Shady, P. Anderson

If Invention has been discussed with or disclosed to external third parties, give details:

Discussed with GM

Witness Statement:

"On the date beside my signature, I read and understood the above invention"

Name: ....

Signature: ....

Date: ....

TITLE A. G. **PROJECT NO.** 17

BOOK NO. EXHIBIT "B"

File Name: 1875_017 (1.6%Pt-CeO2 TPC copp NaOH)
Catalyst prep: N. Trusty/ A. Ghenciu

Objective WGS Catalyst: Prepare 1.6%Pt-CeO2 by coprecipitation, using TPC and Ce(III) nitrate, % metal is by weight.

MATERIALS (shows actual weights used)

Tetramino-Platinum Chloride (TPC), JM stock solution, Lot # 689-691730-01B, 119.58 g Pt/ l sol (105.40 g Pt/ kg sol, d = 1.1345 g/ml) ....1.9 g
Ce(NO3)3 stock solution, JM, 395 g Ce/l, d=1.7 g/ml ....42.95 g (~25.3 ml)
NaOH pellets ....9.1 g
Deionized (DI) water (not including the water for washing the precipitate) ....1.175 l

Calculations Calculated for 12.5 g 1.6%Pt/CeO2 final material, containing:
12.3 g CeO2 and 0.2 g Pt

1. TPC solution needed for 0.2 g Pt:
   0.2 * 1000 / 105.40 = 1.8975 g TPC solution
2. Ce (III) nitrate solution needed for 12.3 CeO2 in the final material:
   moles CeO2 = 12.3 / 172.12 = 0.071462 = moles Ce
   amount Ce = 0.071462 * 140.12 = 10.0132 g
   Ce(III) solution = 7.978 * 1000 / 395 = 25.35 ml Ce solution, or 25.35 * 1.7 = 43.095 g Ce solution
3. NaOH solution needed, 5% excess:
   3 moles/ 1 mol Ce (III) solution, 2 moles/ 1 mol Pt solution
   3 * 0.071462 = 0.2144 moles NaOH for Ce
   2 * (0.2 / 195.09) = 0.00205 moles NaOH for Pt
   Total moles NaOH = 0.21644 moles; with 5% excess, 0.22726 moles NaOH
   NaOH needed: 0.22726 * 40 = 9.1 g

Preparation The weighed amount of TPC and Ce(III) solutions were brought to 100 ml volume with DI water in an Erlenmeyer flask. The weighed amount of NaOH was dissolved into 1.1 liter DI water (~0.2N solution) and transferred to the reactor.

The coprecipitation was conducted at 90°C in a 3-liter glass reactor having a heating/cooling mantle, under vigorous stirring, by dosing the Pt and Ce solution during ca. 1 hr, subsurface. The pump dial was set at "Other," display 0.5 in the beginning followed by 2.5-2.7. During the precipitation, the color changed from light purple (in the beginning) to light yellow - white. The final pH was 8 (pH paper). After the addition of the precursor solution was complete, the precipitate was cured under stirring for ca. 1 hr at 90°C.

The precipitate was filtered and washed repeatedly with a total of 4.6 liter hot DI water (~55-60°C) to filtrate pH 6. The washing step included slurring (redispersing) the precipitate into hot water (85-90°C) with stirring, followed by filtration. The conductivity of the filtrate was not measured.

After filtration, the material was placed in a crucible and dried overnight (~15 hr) at ~125°C in an oven, static air. The dried material was calcined the second day in static air at 500°C for 2 hr. The catalyst was stored in a vial and labeled 1875-017. For WGS testing, the powder was pressed to 15 tons and sieved to 45-60 mesh.

Observations The color change from purple to white during the precipitation should be further investigated. It may depend on the Pt precursor, or it may have been due to impurities in the reaction vessel.

Work continued to Page

SIGNATURE A Ghenciu DATE WITNESS DATE

DISCLOSED TO AND UNDERSTOOD BY N Trusty

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Results & Analytical After drying overnight, 6.12 g material was recovered). No weight loss was recorded after calcination.

Pt%	Ce%	Ce(III)/ Ce(IV)	SA, m2/g	Pore Volume, cc/g	Pore Size Distribution	SEM	TEM	XRD	TPR/ TPO	Pulse Chemi-sorption	ITK	Other

A6.

TITLE **PROJECT NO.** 19

BOOK NO. A.G.

File Name 1875_019 (2%Pt-CeO2-ZrO2 58-42 copp NaOH)
Tested as 1875-A
Catalyst prep: A. Ghenciu N. Trusty

Objective WGS Catalyst: Prepare 2%Pt-CeO2-ZrO2 (CeO2:ZrO2 = 58:42, wt%) by coprecipitation, using nitrate precursors; % metal is by weight.

MATERIALS (shows actual weights used)

Pt nitrate solution, JM, 233.42 g Pt/l sol, 149.33 g Pt/ kg sol, d = 1.5631 g/ml ....2.70 g
Ce(NO3)3 stock solution, JM, 395 g Ce/l, d=1.7 g/ml ....40.0 g (~23.5 ml)
ZrO(NO3)2 stock solution, JM, 203 g/l, d = 1.433 g/ml ....44 g (30.7 ml)
NaOH pellets..........15.0 g
Deionized (DI) water (not including the water for washing the precipitate) ....~1000 ml

Calculation Calculated for 20 g 2%Pt-CeO2 final material, containing:
19.6 g CeO2-ZrO2 and 0.4 g Pt

1. Pt nitrate solution needed for 0.4 g Pt:
   0.4 * 1000 / 149.33 = 2.6786 g Pt solution (1.7137 ml)

2. Ce (III) nitrate solution needed:
   for 58% CeO2, 11.368 g CeO2 in the final material
   moles CeO2 = 11.368 / 172.12 = 0.066047 = moles Ce
   amount Ce = 0.066047 * 140.12 = 9.2545 g
   Ce(III) solution = 9.2545 * 1000 / 395 = 23.4291 ml Ce solution, or 23.4291 * 1.7 = 39.8295 g Ce solution

3. ZrO^{2+} solution needed:
   for 42% ZrO2, 8.232 g ZrO2 in the final material
   moles ZrO2 = 8.232 / 123.224 = 0.066805 = moles Zr
   amount Zr = 0.066805 * 91.224 = 6.09423 g
   ZrO^{2+} solution = 6.09423 * 1000 / 203 = 30.0209 ml ZrO^{2+} solution, or 30.0209 * 1.433 = 43.0199 g ZrO^{2+} solution

4. NaOH solution needed, 10% excess:
   3 moles/ 1 mol Ce (III) solution, 2 moles/ 1 mol ZrO^{2+} solution, 2 moles/ 1 mol Pt solution
   3 * 0.066047 = 0.19814 moles NaOH for Ce(III)
   2 * 0.066807 = 0.13361 moles NaOH for ZrO^{2+}
   2 * (0.4 / 195.09) = 0.004101 moles NaOH for Pt
   Total moles NaOH = 0.33585 moles; with 10% excess. 0.36943 moles NaOH
   NaOH needed: 0.36943 * 40 = 14.78 g

Preparation The weighed amounts of Pt solution, Ce(III) solution, and zirconyl solution were mixed in an Erlenmeyer flask. The weighed amount of NaOH was brought to a 1-liter solution with DI water, in a volumetric flask (0.375N NaOH solution obtained), then transferred to the reactor.

The coprecipitation was conducted at 90-95°C in a 1.5-liter glass reactor having a heating/cooling mantle, under vigorous stirring, by dosing the Pt - Ce - Zr nitrate solution during 25 min , subsurface. The pump dial was set at "Other," display 0.5 in the beginning, then at 2.0. During the entire course of reaction, the color of the precipitate was light yellow-beige. The initial pH (NaOH solution) was 12.5-13 (pH paper). The final pH was not measured. After the addition of the precursor solution was complete, the precipitate was cured under stirring for ca. 1 hr at 90°C, then let stand overnight.

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Work continued to Page

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Second day, the precipitate was filtered and washed repeatedly with a total of ~ 6 liter hot DI water (~55-60°C) to filtrate pH
The washing step included slurring (redispersing) the precipitate into hot water (85-90°C) with stirring, followed by filtration.
conductivity of the filtrate was not measured.

After filtration, the material was placed in a crucible and dried overnight (~ 15 hr) at ~125°C in an oven, static air. The dried material was calcined the second day in static air at 500°C for 2 hr. The catalyst was stored in a vial and labeled 1875-019 (18 A). For WGS testing, the powder was pressed to 15 tons and sieved to 45-60 mesh.

Observations

Results/ Analytical

Pt %	Ce %	Ce(III)/ Ce(IV)	Zr %	SA, m2/g	Pore Volume, cc/g	Pore Size Distribution	SEM	TEM	XRD	TPR/ TPO	Pulse Chemisorption	ITK	Oth

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TITLE A. G.

PROJECT NO.
BOOK NO.

File Name: 1875_021 (3%Pt-CeO2-ZrO2 56-44 copp NaOH)
Tested as 1875-B
Catalyst prep: A. Ghenciu/ N. Trusty

Objective WGS Catalyst: Prepare 3%Pt-CeO2-ZrO2 (CeO2:ZrO2 = 56:44, wt%) by coprecipitation, using nitrate precursors; % metal is by weight.

MATERIALS (show actual weights used)

Pt nitrate solution, JM, 233.42 g Pt/l sol, 149.33 g Pt/ kg sol, d = 1.5631 g/ml .... 13.4 g
Ce(NO3)3 stock solution, JM, 395 g Ce/l, d=1.7 g/ml .... 120 g (~71 ml)
ZrO(NO3)2 stock solution, JM, 203 g/l, d = 1.433 g/ml .... 145 g (~101 ml)
NaOH pellets .... 44.0 g
Deionized (DI) water (not including the water for washing the precipitate) .... ~2000 ml

Calculation Calculated for 67 g 3%Pt-CeO2-ZrO2 final material, containing:
65 CeO2-ZrO2 and 2 g Pt

1. Pt nitrate solution needed for 2 g Pt:
   2 * 1000 / 149.33 = 13.3932 g Pt solution (8.568 ml)

2. Ce (III) nitrate solution needed:
   for 56% CeO2, 36.4 g CeO2 in the final material
   moles CeO2 = 36.4 / 172.12 = 0.21148 = moles Ce
   amount Ce = 0.21148 * 140.12 = 29.6326 g
   Ce(III) solution = 29.6326 * 1000 / 395 = 75.02 ml Ce solution, or 75.02 * 1.7 = 127.533 g Ce solution

3. ZrO^{2+} solution needed:
   for 44% ZrO2, 28.6 g ZrO2 in the final material
   moles ZrO2 = 28.6 / 123.224 = 0.2321 = moles Zr
   amount Zr = 0.2321 * 91.224 = 21.1729 g
   ZrO^{2+} solution = 21.1729 * 1000 / 203 = 104.3 ml ZrO^{2+} solution, or 104.3 * 1.433 = 149.462 g ZrO^{2+} solution

4. NaOH solution needed, no excess:
   3 moles/ 1 mol Ce (III) solution, 2 moles/ 1 mol ZrO^{2+} solution, 2 moles/ 1 mol Pt solution
   3 * 0.21148 = 0.63444 moles NaOH for Ce(III)
   2 * 0.2321 = 0.4642 moles NaOH for ZrO^{2+}
   2 * (2 / 195.09) = 0.020503 moles NaOH for Pt
   Total moles NaOH = 1.11914 moles;
   NaOH needed: 1.11914 * 40 = 44.77 g

Preparation The weighed amounts of Pt solution, Ce(III) solution, and zirconyl solution were mixed in an Erlenmeyer flask. The weighed amount of NaOH was brought to a 2-liter solution with DI water, in a volumetric flask (0.5N NaOH solution obtained), then transferred to the reactor.

The coprecipitation was conducted at 90-95°C in a 3-liter glass reactor having a heating/cooling mantle, under vigorous stirring, by dosing the Pt - Ce – Zr nitrate solution during ca. 1 hr, subsurface. The pump dial was set at "Other," display 0.5 in the beginning, then at 2.0, then the dosing accelerated to 3.0 pump dial. During the course of reaction, the color of the precipitate intensified from light yellow-beige to brown.

After the addition of the precursor solution was complete, the precipitate was cured under stirring for ca. 1 hr at 90°C, then let stand overnight. An additional 10 g solution NaOH (3 g pellets) was added before the stirring was stopped. The final pH was 8.

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SIGNATURE A Ghenciu

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Second day, the precipitate was washed and filtered repeatedly with a total of ~ 12 liter hot DI water (~55-60°C) to a filtrate pH [illegible] 6. The washing step included slurring (redispersing) the precipitate into hot water (85-90°C) with stirring, followed by filtration. The conductivity of the filtrate was not measured.

After filtration, the material was placed in a crucible and dried overnight (~15 hr) at ~125°C in an oven, static air. The dried material (color dark brown) was calcined the second day in static air at 500°C for 2 hr. The catalyst was stored in a vial and labe[illegible] [illegible] the powder was pressed to 15 tons and sieved to 45-60 mesh.